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Electron spin resonance studies of γ-irradiated simple formates

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The present paper reports the result of esr investigation of γ-irradiated divalent formates namely, barium, magnesium and cadmium formates at room temperature. The investigation reveals that the irradiated samples at room temperature, in general, yield $\dot{C}O^-_2$ radicals trapped in the lattice. The subsequent heat treatment of the irradiated samples yields new radicals having chemical structure $O_2C\,O\,\dot{C}HO^-$ at the cost of $\dot{C}O^-_2$ radicals. The decay mechanism of $\dot{C}O^-_2$ has been suggested. The principal g-values of $\dot{C}O^-_2$ radical and H(C) coupling tensor of $O_2C\,O\,\dot{C}HO$ have been evaluated for these samples.

1 Introduction

Recent electron spin resonance (esr) study (Ovenall & Whiffen 1961) on γ-irradiated sodium formate reveals that when single crystals of sodium formate are irradiated with γ-rays at room temperature free radicals having chemical structure $\dot{C}O^-_2$ are trapped. Later studies on some γ-irradiated formates viz. lithium, potassium, magnesium and barium formates by Atkins *et al* (1962) further reveal that similar radicals are also found to be trapped in those systems. It is thus generally believed that γ-irradiation of formates at room temperature would produce $\dot{C}O^-_2$ radicals. The main feature of esr spectra of such a radical is a singlet with some characteristic broadening due to g-anisotropy if examined in polycrystalline or in powder form. However $\dot{C}O^-_2$ trapped in $NaHCO_2$ and $KHCO_2$ gives a quartet spectra due to hyperfine interaction of ^{23}Na and ^{39}K nuclei of spin 3/2, hyperfine splittings being 8·2 and 7 gauss respectively (Ovenall & Whiffen 1961, Atkins *et al* 1962). On the other hand esr spectrum in γ-irradiated barium formate attributed to $\dot{C}O^-_2$ radical by Atkins *et al* consists of a triplet having separation of ~24 gauss between the outer lines. But hitherto little attention has been given to this peculiar feature of the esr spectra of irradiated barium formate. The triplet feature of the spectra can not be explained in terms of the $\dot{C}O^-_2$ radical only.

Recent esr studies on γ-irradiated sodium formates (Bellis & Clough 1965) show that the irradiated crystals undergo an irreversible change on heating to 180°C yielding a new radical trapped in a specific lattice orientation.

Keeping these facts in mind we thought it advisable to re-examine the esr spectra of γ-irradiated barium formates afresh along with similar divalent formates like magnesium and cadmium formates. The result of our study is reported here.

2 Experimental

We studied the esr spectra of γ-irradiated barium formates both in single crystal and in polycrystalline forms. On the other hand magnesium and cadmium formates were studied in the polycrystalline form only.

Single crystals of barium formates were grown from saturated aqueous solution by slow evaporation. A few small well grown crystals with well developed faces were chosen for our purpose. The morphological habit of growth of the crystal was found to be the same as has been reported by Groth (1910). The unit cell has orthorhombic symmetry as reported by Groth, with axial ratios $a : b : c = 0{\cdot}7650 : 1 : 0{\cdot}8638$. The faces were identified by measuring interfacial angles with a single circle conventional goniometer and comparing these with those reported by Groth. The prominent faces those were found to grow are : $m(110)$, $r(101)$, $b(010)$, $q(011)$ etc.

2.1. *Preparation of samples*

Finely powdered barium, magnesium and cadmium formates (Annalar grade of BDH) were poured in specially constructed quartz sample tubes lower part of which, containing the powder samples, are made of spectrosil tubings of ~3 mm outer diameter. The sample tubes were then evacuated and sealed off at a pressure of 10^{-6} mm Hg. The barium formate crystals were also sealed off in thin walled pyrex tubes. The samples were then irradiated with ^{60}Co source for about 12 hrs giving a total radiation dose of 0·5 MR approximately. A few samples were irradiated for shorter periods between 3–4 hours.

2.2. *Recording of ESR Spectra*

The esr spectra of the irradiated samples were recorded with a Varian EPR Spectrometer, V4500 using a multipurpose cavity, the modulation frequency of the cavity being 100 KHz.

For recording single crystal spectra at various orientations with respect to the direction of the static magnetic field a conventional type of laboratory made goniometric device was used. The device consists of a thin perspex rod lower part of which is suitably machined to hold a small crystal in a desired orientation. The upper part of the rod is rigidly fixed to a graduated disc between

0–360° at 2° intervals so that the crystal can be rotated around a vertical axis with respect to a fixed external marker attached to the cavity

The esr spectra were calibrated in terms of the magnetic field using a proton magnetometer (PMKII) supplied by Newport Instruments. The resonance frequency was measured with the help of a microwave frequency meter supplied by Hewlett-Packard

3. Results

3.1. *Barium formate*

Powder samples : The esr spectra of γ-irradiated powder samples recorded just after irradiation show a strong singlet having characteristic g-anisotropy (Figure 1a) The samples which are irradiated for 12 hrs (~0·5 MR) showed

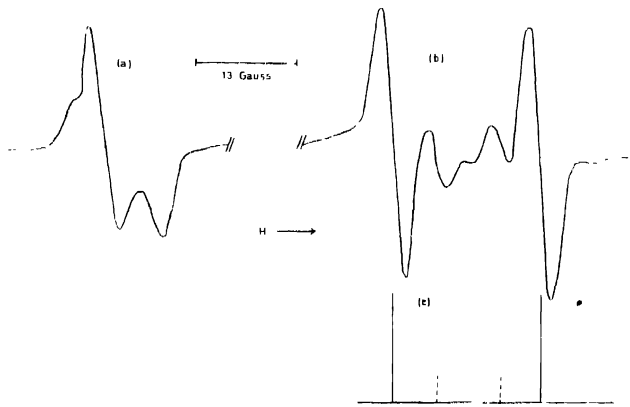

Fig 1. Esr spectrum of γ-irradiated (a) polycrystalline barium formate immediately after irradiation (b) single crystal of barium formate with H_{11} c-axis after heat treatment, the vertical lines indicate the positions of the theoretically computed lines (dotted lines indicate the position of forbidden lines), experimental lines occur at 3369.11 G., 3374.47 G., 3382 74 G and 3388.11 G

two outer lines separated by about 17 gauss at very high gain The samples irradiated for shorter period (3–4 hours) showed only a singlet spectrum and no traces of a doublet was observed even at very high gain The line shape of the singlet from all the irradiated powder samples was found to be similar The principal values of g-tensor of all the samples were estimated from the line shape following the method suggested by Atkins & Symons (1967). Principal values of g-tensor of all the samples were found to be the same within the experimental error These have been shown in table 1. Comparison of the principal

values obtained by us with those attributed to CO_2^- radical by others clearly show that this radical has structure CO_2^- formed by the scission of C–H bond of barium formate molecule

Table 1 Summary of the observations of polycrystalline samples of γ-irradiated formates at room temperature immediately after irradiation

System	Radical trapped at room temp	Principal g-values			References
Barium formate $Ba(HCOO)_2$	CO_2^-	2·0032 ± (·0005)	1·9974 ± (·0005)	2·0013 ± (·0005)	Present work
Cadmium formate $Cd(HCOO)_2$	CO_2^-	2·0073 ± (·0005)	1·9969 ± (·0005)	2·0011 ± (·0005)	"
Magnesium formate $Mg(HCOO)_2$	CO_2^-	2·0033 ± (·0005)	1·9974 ± (·0005)	2·0017 ± (·0005)	"
Sodium formate $NaHCOO$	CO_2^-	2·0032	1·9975	2·0017	(Ovenall & Whiffen 1961)
Calcium carbonate $CaCO_3$	CO_2^-	2·0032	1·9973	2·0016	(Marshall *et al* 1964)

The samples were then left at room temperature for 24 hours and examined. The esr spectra of all these samples showed a marked change The spectra consist of three lines of almost equal intensity However the position of the central line is the same as that of the singlet We therefore conclude that the central line is the same as the singlet although its intensity has decreased considerably The separation of the outerlines remained unchanged for all samples. It is suggested that outer lines are due to a doublet originating from a new radical formed by the decay of the CO_2^- reacting with a parent formate ion

The samples were then slowly heated above room temperature and recooled to room temperature It is observed that the intensity of the singlet decreases further and the intensity of the outer lines increases This conclusively proves that the outer lines are due to a new radical formed by the reaction of CO_2^- with a parent formate ion Finally when the samples were heated to 165°C and re-examined at room temperature the singlet completely disappeared leaving the doublet of separation ~17 gauss

Analysis of single crystal spectra The γ-irradiated single crystal of barium formate with c-axis parallel to the magnetic field gave a singlet when examined just after irradiation After keeping the crystal at room temperature for 24 hours, we noted similar change as was obtained in the case of powder samples i.e., the spectra consist of three lines, the separation between the outer lines being ~19 gauss The position of the central line was found to be the same

as the singlet. The crystal was then, as before, gradually heated above room temperature by 5°C intervals and examined at room temperature. As in the powder samples, the singlet gradually decreases in intensity whereas the outer lines increase in intensity. Finally when heated to 165°C the esr spectra become a doublet of separation ~19 gauss (Figure 1b).

In order to identify the nature of the radical giving a doublet detailed esr spectra at various orientations were recorded. The reference system xyz, chosen were the crystallographic abc axes. $a-b$, $b-c$ and $c-a$ planes were explored by rotating the crystal around c, a and b axes respectively at 20° intervals. When the crystal axes were set parallel to the field doublet spectra were obtained. The doublet splittings were found to be 17·80±1, 18·00±1 and 19·00±1 gauss when the field was set parallel to a, b, c axes respectively. In all three planes the doublet separation was found to vary considerably with orientation. Two magnetically distinguishable sites related by orthorhombic symmetry were found when the bc and ca planes were explored. However no site splittings were observed when ab plane was explored. The range of variation of the hyperfine splittings clearly shows that a proton interacting with the unpaired electron of the species must be in an alpha position. Although the strong doublets dominated the esr spectra we also observed the so-called 'forbidden lines' in some orientations.

Interpretation of the spectra. As already mentioned the magnitude and range of variation of the doublet splittings clearly indicate that the hyperfine splittings must have originated from an α-proton interaction. The esr spectra were interpreted in terms of the spin Hamiltonian

$$\mathcal{H} = \beta \boldsymbol{S}\,\boldsymbol{g}.\boldsymbol{H} + \boldsymbol{S}\,\boldsymbol{A}\,\boldsymbol{I} - g_n\beta_n \boldsymbol{H}\,\boldsymbol{I} \qquad (1)$$

Here the first term represents the Zeeman interaction energy between the unpaired electron spin and the magnetic field, the second is the hyperfine interaction between the electron spin and the nuclear spin and the last term represents the direct interaction between a proton and the magnetic field. Tensor $\boldsymbol{A}$, a symmetric tensor of rank two, describes the coupling of the proton and the unpaired electron spin.

Although eq. (1) is suitable for calculating energy levels and possible transition frequencies between various levels once $\boldsymbol{A}$ is known, but the reverse process i.e. to evaluate the elements of $\boldsymbol{A}$ tensor from eq. (1) using experimentally observed hyperfine splittings is not simple. In order to evaluate the tensor elements of $\boldsymbol{A}$ on an approximate basis we first neglect the last term in eq. (1), whose effect is primarily, to relax the selection rule $\Delta M_I = 0$ and is seldom encountered at x-band frequencies. Then eq. (1) becomes

$$\mathcal{H} = \beta \boldsymbol{S}.\boldsymbol{g}\,\boldsymbol{H} + \boldsymbol{S}.\boldsymbol{A}.\boldsymbol{I}. \qquad (2)$$

Assuming the high field approximation and g nearly isotropic which is true for organic free radicals we have evaluated the approximate principal values of the $\boldsymbol{A}$ tensor and its elements with respect to crystallographic *abc* axes on the basis of the spin Hamiltonian represented by eq (2) (Morton 1964)

However these principal values of $\boldsymbol{A}$ tensor and its elements in *abc* axes would be approximate as we have neglected the third term in eq (1) whose effect would be to relax the selection rule $\Delta M_I = 0$ causing the appearance of the so-called forbidden transitions in many orientations If we include the third term in eq (1), we may get four transition lines, with respect to the central resonance field, for a single proton hyperfine interaction The relative intensity of the outer and inner doublets may be evaluated from their respective transition probabilities (Lefebvre & Maruani 1965) Using these approximate tensor elements the splittings of outer and inner doublets and their relative intensities have been evaluated theoretically in terms of the Hamiltonian of eq (1). The

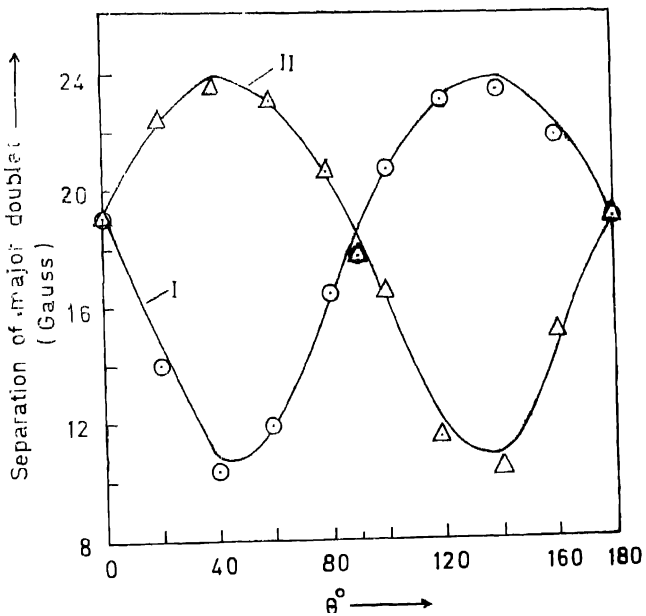

Fig. 2. Variation of separation of major doublets of two radical sites I and II in c-a plane; θ measures the angle between c-axis and H; ⊙, △ denote experimental points of sites I and II respectively. — denotes theoretically computed curves. All experimental points are within experimental error of ±0.5 Gauss

observed splittings were then compared with the theoretically calculated splittings. The tensor elements were then readjusted to get the best fit between the theoretically calculated and experimentally observed splittings within experimental errors (Whiffen 1961) The finally adopted Tensor $\boldsymbol{A}$ is shown in table 2 with their principal values and direction cosines with respect to *abc* axes The comparison between the theoretically calculated and observed splittings of the strong doublet is shown in figure 2 for *c–a* plane

3.2 : *Cadmium and magnesium formates*

γ-irradiated polycrystalline samples of cadmium and magnesium formates gave characteristic asymmetric singlet spectra (Figures 3a and 3c) as in the case

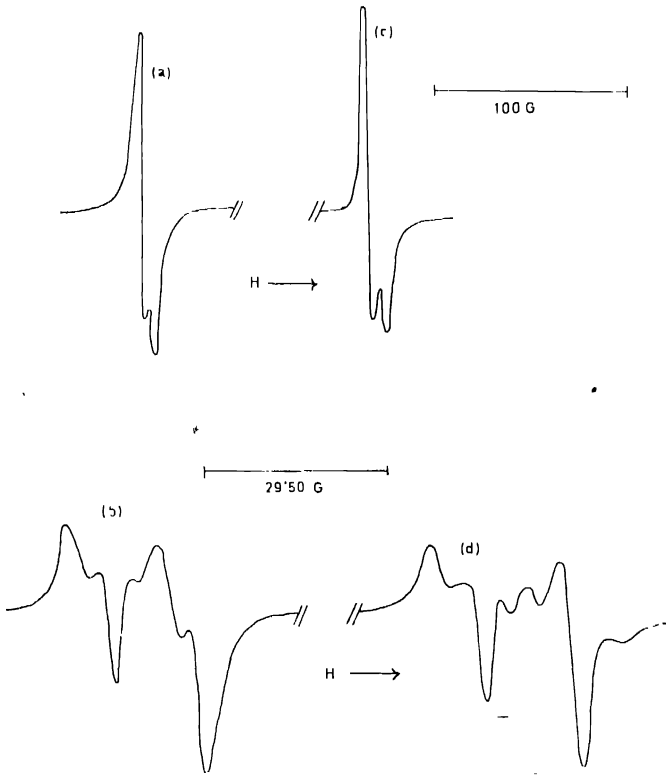

Fig. 3. Esr spectrum of γ-irradiated polycrystalline (a) cadmium formate and (c) magnesium formate immediately after irradiation; esr spectrum of γ-irradiated (b) cadmium formate and (d) magnesium formate after heat treatment.

of barium formate, just after γ-irradiation at room temperature. The g-values estimated from characteristic line shapes show similar values as obtained from barium formate spectra (table 1). The singlets obtained from cadmium and magnesium formates may therefore safely be attributed to the same type of radical i.e., CO^-_2. No traces of doublet was however observed even at very high gain with any of the irradiated samples.

The samples when examined again after keeping them at room temperature did not show any change. The samples were then gradually raised to higher temperature and then recooled to room temperature for examination. In the case of cadmium formate the singlet due to CO^-_2 gradually decreases and at 135°C the doublet begins to appear. At 140°C a well resolved asymmetric doublet showing characteristic hyperfine anisotropy is observed (figure 3b) and the singlet completely disappears. The yield of radicals is however much poorer than in the case of barium formate. Magnesium formate also behaved in a similar manner except that the yield is still poorer and the singlet completely disappears at 185°C leaving a doublet of same character (figure 3d) as those of cadmium and barium formates.

The approximate values of the principal values of the $\boldsymbol{A}$ tensor were evaluated from the line shape of the polycrystalline spectra for both the samples. These values are shown in table 2 along with those for barium formate.

4. Discussion

There seems little doubt regarding the identification of initial radical giving a singlet. The comparison of g-values with the accepted values for CO^-_2 radical (table 1) clearly shows that the radical has structure CO^-_2 formed by the scission of C–H bond of a parent formate ion. But the identification of the radical formed at higher temperature poses some problem. It is however certain that the structure of the new radicals formed after heat treatment in three formates under study is similar. It is also certain that the new radical is a subsequent product, and its yield increases with the decay of the radical CO^-_2. This clearly indicates that the new radical is a product of chemical reaction between radical CO^-_2 and a formate ion. The new radical must have one proton interacting with the unpaired electron, thus producing a doublet of isotropic splittings of ~16 gauss, as for example, in barium formate. The corresponding anisotropic components are −9·8, +2·4, +7·3 gauss. The range of anisotropy clearly indicates that the interacting proton can not occupy a β position for which splittings would be almost isotropic. We therefore inclined to believe that the interacting proton is in the alpha position with respect to the p_z orbital of the carbon atom on which the unpaired electron is localized. However, the principal

Table 2 Summary of observations of γ-irradiated formates after heat treatment

System	H(C) hyperfine coupling tensor, A (Gauss)			Principal values (Gauss)	Isotropic values (Gauss)	Anisotropic values (Gauss)	Direction cosines w.r.t Crystallographic *abc* axes		
Barium formate (Single crystal)	* 16·00	−3·20	∓6·86	− (26·2, 14·0, 9·1)	−16·4	−9·8	−0·579	∓0·507	−0·638
	−3·20	16·83	±4·66			−2·4	0·481	∓0·845	−0·234
	∓6·86	±4·66	16·44			±7·3	∓0·658	∓0·172	−0·733
Cadmium formate (Polycrystalline)				− (23·0, 13·0, 7·1)	−14·4	−8·6			
						−1·4			
						−7·3			
Magnesium formate (Polycrystalline)				− (24·2, 12·4, 6·5)	−14·4	−9·8			
						+2·0			
						+7·9			
Sodium formate (Single crystal) (Bellis & Clough 1965)				− (22·3, 14·1, 6·9)	−14·4	−7·9			
						+0·3			
						+7·5			

* The upper and lower signs indicate the two radical sites I & II respectively.

values and the isotropic values obtained by us are somewhat less than the typical values for such an α-proton as observed in other radicals. As for example in the case of irradiated malonic acid the principal values and isotropic value for such an alpha proton are 32·5, 21·8 and 10·4 gauss and 21·8 gauss respectively (Cole & Heller 1961). Compared to these typical values, our values seem to be about three-fourth times less. The possible explanation is, therefore, that the radical contains a $\dot{C}H$ group with a spin density in the carbon p_z orbital approximately of three-fourth of the spin density of malonic acid radical, $(\dot{C}H(CO_2H)_2)$ estimated to be 0·89 (Karplus & Fraenkel 1961). Thus spin withdrawal by other groups attached to a CH fragment is not an unknown phenomenon as has been observed in many systems (Fischer 1965; Dixon & Norman 1964).

About the chemical structure of the radical one cannot reach a definite conclusion. The formation of $\dot{H}CO$, the so-called formyl radical or $\dot{C}OOH$ by reacting $\dot{C}O_2^-$ with a formate ion, $HCOO^-$ could be a possibility. The formation of such a radical however in our case can be ruled out on the following grounds. In the case of $\dot{H}CO$ radical the isotropic splittings will be quite large. In fact it has been observed by Brivati *et al* (1962) that in case of γ irradiation of formaldehyde a $\dot{H}CO$ radical is trapped and the isotropic splitting due to the attached proton is ~136 gauss. This was later confirmed by Adrian *et al* (1962) who have identified $\dot{H}CO$ radical (~137 gauss) formed by the photolysis of $HI : HCHO$ in CO and Argon matrix respectively at 4 K. Again radical assigned to $\dot{H}CO$ in u-v irradiated methanol, as reported by Sullivan & Koski (1963) show hyperfine splitting of H(C) proton as ~130 gauss. On the other hand the structure $\dot{C}OOH$ would have very little isotropic splitting due to the H(O) proton. We, therefore, conclude that the new radical must have been formed by the direct attachment of CO_2^- with a parent formate ion via an oxygen atom of the formate ion and transferring the spin to carbon atom. Thus the structure of the radical is $O_2C\text{-}O\text{-}\dot{C}HO$. Our observation confirms the similar result earlier reported by Bellis & Clough (1965) in the case of γ-irradiated sodium formate.

There is also radiation-chemical evidence in support of our observation and that of Bellis & Clough. Getoff (1963) suggested that during carboxylation of aqueous formic acid in presence of CO_2 when irradiated with γ-rays, similar radical can be formed according to following reaction scheme

$$CO_2^- + HCOO^- \rightarrow CO_2O\text{-}\dot{C}HO$$

We therefore suggest that this type of reaction could also take place in solid phase.

We further note that the yield of new radicals in barium formate is much higher than in cadmium and magnesium formates. Even at room temperature the yield is considerable. These show that in case of barium formate the trapping of CO^-_2 is less stable than in cadmium and magnesium formates. The new radicals are found to form in cadmium and magnesium formates only in higher temperature. We therefore infer that most of the formates when irradiated with γ-rays would yield initially CO^-_2 radicals which when heated to above room temperature, would produce new radicals of the type CO^-_2-O-$\dot{C}$HO$^-$. The reaction mechanism of the formation and decay of $\dot{C}O^-_2$ in formates may therefore be summarised as follows

$$HCO^-_2 \xrightarrow[\text{heat}]{\ldots} \dot{C}O_2 + H$$

$$CO^-_2 + HCO^-_2 \longrightarrow CO^-_2\text{-O-}\dot{C}HO$$

$$\dot{C}O_2 + \dot{C}O^-_2 \rightarrow C_2O_4^- \quad \text{(oxalate)}$$

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